ARIZONA DEPARTMENT
OF
ENVIRONMENTAL QUALITY

Douglas A. Ducey
Governor

Misael Cabrera
Director

via e-mail

April 20, 2016
FPU16-230

Ms. Catherine Jerrard
AFCEC/CIBW
706 Hangar Road
Rome, NY 13441

RE: WAFB – ADEQ Comments – ST012 - *Draft Final Addendum #2 Remedial Design and Remedial Action Work Plan for Operable Unit 2 [OU2] Revised Groundwater [GW] Remedy, Site ST012, Former Williams Air Force Base, Mesa, Arizona*; prepared for Air Force Civil Engineer Center AFCEC/CIBW, Lackland AFB, Texas; prepared by Amec Foster Wheeler Environment & Infrastructure, Phoenix, Arizona (Amec); document dated March 15, 2016

AND

ADEQ Evaluation of Response to Comments (RTCs) in regard to *Draft Addendum #2 Remedial Design and Remedial Action Work Plan for Operable Unit 2 [OU2] Revised Groundwater [GW] Remedy, Site ST012, Former Williams Air Force Base, Mesa, Arizona*; AMEC document dated November 30, 2015; (as presented in *Appendix I – Response to EPA and ADEQ Comments* of the Amec Draft Final document dated March 15, 2016).

Dear Ms. Jerrard:

Arizona Department of Environmental Quality (ADEQ) Federal Projects Unit (FPU) and ADEQ contractors reviewed the referenced documents. Comments and evaluations are provided are provided below. The letter format will be presented in following order:

- I. Draft Final-related General Comments
- II. Draft Final-related Specific Comments
- III Evaluation of Response to Comments

The Response to Comment evaluations are generally presented in the order of (a). ADEQ evaluation, (b). the Air Force response, and (c). the initial regulatory comment. The comment and response to comment replication purpose is to provide this document content completeness.

I. Draft Final General Comments:

1. Please clarify throughout the document that the sulfate is being added to stimulate the subsequent microbial degradation of hydrocarbons. The response to EPA Specific Comment 42, as well as similar quotes found throughout the document text and appendices, erroneously suggests that sulfate ions alone will abiotically degrade hydrocarbons.

2. The term "sulfate degrading bacteria" and "sulfate degradation" are improper and should be corrected throughout the document to "sulfate-reducing bacteria" and "sulfate reduction."

3. Bio-traps are a copyrighted name, and as such, the "B" should be capitalized, and name is also hyphenated. Please correct this throughout the document.

4. The abbreviation qPCR is variously referred to as "quantifiable polymerase chain reaction", "qualitative polymerase chain reaction", and "quantified polymerase chain reaction". The correct term is "quantified polymerase chain reaction". Please correct this throughout the report.

5. Please clarify how chloride concentrations are not expected to inhibit or slow EBR at this site. Chloride levels appear to be extremely high, and may inhibit some sulfate-reducing bacteria as well as others that are hoped to be used for target compound biodegradation during the EBR phase.

6. Please clarify why sulfate should be added to a system that currently has sulfate levels in tested wells as high as 310 mg/L.

7. Please clarify how this site geochemistry suggests the presence of a robust indigenous sulfate-reducing population. If sulfate-reducing bacteria were a robust population at this site, sulfate concentrations would be expected to be highly depleted. However, concentrations are very high, suggesting a lack of sulfate utilization (and thus a lack of indigenous sulfate-reducing bacteria).

8. ADEQ continues to request the installation of additional monitoring wells to characterize the full extent of NAPL east of the SEE treatment area, and dissolved-phase constituents exceeding the ROD remedial goals east, northeast, and north of the site. Specifically, additional wells should be installed north of well W36, northeast of well W34, and east of Sossaman Rd. between wells W24 and W38.

II. Draft Final Specific Comments:

1. **Section 2.4, lines 522-527.** See the evaluation of the response to ADEQ General Comment 2. The referenced EBR Field Test, along with 18-year-old geochemical data, is not enough to conclusively determine that sulfate-reduction will be the dominant microbial process for EBR. Only after the site has cooled enough for proper geochemical and microbial sampling can this be accurately determined.

2. **Section 2.4, lines 527-528.** Please clarify the statement that, "sulfate amendment can either be used solely or in combination with aerobic methods to achieve remediation goals." The use of sulfate to stimulate the strongly anaerobic process of sulfate-reduction is not compatible with aerobic methods of bioremediation. Sulfate reduction occurs only under highly reduced environmental conditions, while aerobic respiration occurs only under highly oxidized environmental conditions. Thus, sulfate-reduction cannot be used in combination with aerobic methods.

3. **Section 3.1.3, Line 625.** Please correct and clarify the statement, "natural site conditions are predominantly based on the activity of sulfate-reducing bacteria." Site biogeochemical conditions are not based on the activity of the indigenous bacteria. Rather, the members of the indigenous bacterial population and their activity is based on, and determined by, site biogeochemistry.

4. **Page 3-2, Lines 626-628.** See the evaluation of the response to ADEQ General Comment 1. The statement assumes *a priori* knowledge that does not appear to exist regarding the indigenous microbial population. Furthermore, this statement assumes that sulfate-reducers dominate the indigenous population – something that has not been proven. ADEQ has specifically questioned and asked to have this investigated.

5. **Page 3-5, Line 728.** What specific "rate-limiting geochemical conditions" will be monitored, and what is the plan for maintaining effective EBR if one of these adverse conditions is encountered?

6. **Page 3-7, Lines 826-827.** The statement "...other compounds will degrade and consume sulfate in the process" is not accurate. Please revise this to "Indigenous microbes will consume sulfate while degrading compounds other than those targeted".

7. **Section 4.2.2.** Please detail how both population surge/crash and plugging of the formation with biomass will be prevented.

8. **Section 4.2.3, Micronutrient Dosing:**

a. Please detail a correct micronutrient monitoring schedule, as well as all micronutrient components that must be monitored. Although some micronutrients are listed in this section, the most common one to deplete (even for sulfate-reducers) is bioavailable nitrogen. This nitrogen is critical, as it is the basis of DNA, RNA, all proteins, and many other biomolecules. Bioavailable nitrogen can quickly stall all bioattenuation if lacking, and its concentrations must be monitored before any TEA addition as well as regularly during the EBR event. Failure to properly monitor micronutrient concentrations during the multi-year EBR event can result in early and undetected failure of EBR.
b. Please describe the components of the suggested Bionetix MICRO 14 amendments.
c. Please describe how decisions will be made regarding which possible micronutrient additions will be made, how decisions about the actual delivery method and concentration will be made, and what type of subsurface monitoring will be conducted to ensure a beneficial impact on COC bioattenuation.

9. **Section 4.2.5.** Please describe plans to monitor and prevent biofouling of the formation.

10. **Section 5.1.1.** Please develop and explain a plan to monitor the indigenous microbial population to determine if EBR will be successful. Please detail how EBR microbial data will be compared to pre-EBR microbial data.

11. **Page 5-8, Lines 1326-1328.** The plan states that "microbes will be analyzed to determine if indigenous sulfate reducers are mineralizing and incorporating the COCs into their biomass". This is a misleading statement regarding the capabilities of the SIP samplers and the data they will provide. Although the Bio-trap analysis will be able to confirm if indigenous microbes have degraded target compounds, this

technology will not be able to confirm the identity of the organism (or the identity of the class of organism, such as sulfate-reducers) responsible for this biodegradation. Instead, the SIP samplers will only be able to confirm that some type of indigenous microbe may have degraded target COCs.

Furthermore, by isolating DNA from the SIP samplers in order to run a qPCR on sulfate-reducing bacteria, the only data obtained from this action will be to quantify the sulfate-reducing population from within the SIP samplers. This will still not confirm that these sulfate-reducing bacteria are, in fact, responsible for target-compound biodegradation. Furthermore, this qPCR will quantify the SRB population found within the SIP sampler – a sampler which is designed to be somewhat a mimic of the natural environment but not an exact replica. Thus, the qPCR data is arguably of a more qualitative nature and not truly a quantitative nature.

12. **Section 6.1.** It is stated that EBR will continue until conditions are such that monitored natural attenuation will be able to take over as the remediation pathway of choice. Please detail how this EBR endpoint will be determined, and please include what variables will be monitored as part of this determination.

III. Evaluation of Response to Comments

Evaluation 1: ADEQ Evaluation of Air Force March 15, 2016 Response:
The proposed SIP and qPCR analyses do not address the ADEQ request to determine if non-sulfate-reducing bacteria play a significant role in the degradation of site constituents. The response, as well as the referenced Table 5-1, indicates that SIP and qPCR analyses will be performed to monitor the sulfate-reducing community only. Please address the ADEQ request to evaluate the presence of non-sulfate-reducing bacteria.

Replication of Air Force Response to Comment 1 (reference Mar. 15, 2015):
The addition of SIP within each of the hydrostratigraphic zones has been added to the monitoring plan. An entry was added to Table 5-1 detailing sample type and frequency, and a narrative was added to Section 5.4 – Groundwater Monitoring Well Sampling, as discussed below in General Comment 3. This addition will provide evidence that COCs are being mineralized and incorporated into biomass. SIP analysis results, in combination with COC and TEA sampling and analysis, will provide sufficient data to assess enhanced sulfate reduction at the site. Primary assumptions in natural attenuation assessments and models presented previously for the site (BEM TEE Pilot Test Report, 2011 and Natural Attenuation Report, 1998) consider instantaneous TEA utilization over the volume impacted with petroleum contamination; and, across the primary TEAs, oxygen, nitrate, iron, sulfate, and carbon dioxide. The approach presented previously is widely accepted as a model for natural attenuation; however, it oversimplifies the spatial and temporal distribution of TEA utilization. For instance, aerobic and sulfate reduction do not occur in the same space simultaneously. Naturally available oxygen is depleted rapidly and aerobic biodegradation is predominant at the edges of the plume; anoxic nitrate utilization occurs within a volume that overlaps the inner boundary of predominant oxygen utilization and the outer boundary of metals reduction. So long as the concentration and mass of substrate and petroleum contamination is sufficient to not be rate limiting; methanogenesis will be predominant in some space at the core of the impact, considering flow rate and direction and naturally occurring TEA flux. Natural biodegradation at ST012 follows this process of TEA utilization; and, at some locations and over some volume within the petroleum impacted subsurface, sulfate reduction is the predominant biodegradation pathway for petroleum hydrocarbons. The natural flux of sulfate limits the biodegradation rate of the petroleum hydrocarbon contamination. Similar to enhanced aerobic

biodegradation; it is assume that if the TEA sulfate and petroleum substrate are abundant and available at concentrations that do not limit biodegradation then the sulfate will be utilized to respire the petroleum. The addition of sulfate as proposed in the design will tip the scales in favor of sulfate reduction as the dominant reduction pathway for an area and mass of petroleum impacted subsurface that are much greater than under natural conditions.

> **Replication of ADEQ General Comment 1 (reference ADEQ FPU16-167, Feb. 11, 2016):** ADEQ recommends that additional microbial analyses be performed at various site locations to determine if non-sulfate-reducing bacteria play a significant role in the degradation of site constituents. It is currently unknown if sulfate-reducers are the dominant hydrocarbon-degrading species in the system.

Evaluation 2: ADEQ Evaluation of Air Force March 15, 2016 Response:
Geochemical data should be updated with current values and presented for analysis/evaluation. The referenced data is from a 1998 report, and is possibly no longer relevant due to the extreme impact that the steam treatments may have had on site geochemistry, which is critical to the success of the EBR stage.

Replication of Air Force Response to Comment 2 (reference Mar. 15, 2015):
Groundwater geochemistry for the entire site has been studied and reported previously (BEM, 1998). The geochemistry conditions presented in the BEM report generally show a consistent pattern throughout the source area with some variation in TEA concentration seen along the perimeters. The BEM report demonstrated that most of the electron donors are active at the site with depletion of oxygen, nitrate, and sulfate coinciding with elevated BTEX concentrations. The report also concluded that sulfate flux accounts for about 80% of the naturally occurring assimilative capacity for BTEX.
No changes made.

> **Replication of ADEQ General Comment 2 (reference ADEQ FPU16-167, Feb. 11, 2016):** Groundwater geochemistry results for the entire site should be reviewed to determine if a different terminal-electron acceptor dominates at other site locations. This will help discern if populations other than sulfate reducers are strongly active at the site and significantly impacting the polishing of site constituents.

Evaluation 3: ADEQ Evaluation of Air Force March 15, 2016 Response:
3a) Please detail how the proper length of time for sampler deployment will be determined and followed. The response states that the *Bio-trap*® SIP sampler will be deployed for approximately one month before being retrieved for analysis. However, this is a general timeframe provided by Microbial Insights to be used as a starting point in determining the proper length of deployment time. This time length should be adjusted based on site geochemical conditions and target compounds. If the assumed sulfate-reducing conditions are dominant, then experience with these samplers in anaerobic environments suggests that one month may not be enough time to properly allow for adequate target compound mineralization or conversion to biomass.

3b) Furthermore, referring to the Feb. 11, 2016 Comment 2, the current geochemistry is unclear. To assess the correct time interval that the samplers should be deployed requires an understanding of the current geochemistry.

3c) The response to Comment 3 also states that "…DNA extracts will be analyzed by …qPCR… to identify and quantify sulfate-reducing bacteria." As stated in Comment 2, this will not address the ADEQ request to determine if non-sulfate-reducing bacteria play a significant role in the degradation of site constituents. Please detail how the ADEQ request will be addressed.

Replication of Air Force Response to Comment 3 (reference Mar. 15, 2015):
The application of SIP analysis is considered a viable line of evidence for confirmation that COCs are being biodegraded, mineralized and incorporated into biomass. The following text was added to section 5.4:

"As a means to confirm if COCs are being incorporated into biomass and mineralized through bioremediation, Stable Isotope Probing (SIP) sampling and analysis will be conducted at six monitoring wells, two from each of the three hydrostratigraphic zones. One of the monitoring wells from each of the zones is located in the TTZ. These three wells are ST012-CZ2, ST012- UWBZ24, and ST012-LSZ10. The other three wells selected for SIP sampling and analysis are to evaluate LNAPL impact areas that are outside the TTZ. These three perimeter monitoring wells are ST012-CZ20, ST012 UWBZ31, and ST012-LSZ42. Bio-trap® samplers from Microbial Insights, seeded with synthesized forms of benzene, toluene, ethylbenzene, xylenes, and naphthalene containing carbon isotope 13C, will be placed in each well for approximately one month. The biotraps will be retrieved from the well and the microbes that grew on the bio-trap will be analyzed to determine if indigenous sulfate reducers are mineralizing and incorporating the COCs into their biomass. As part of SIP analysis, two methods will be used to demonstrate biodegradation of the COC:

- *Quantification of 13C enriched phospholipid fatty acids (PLFA), which will indicate incorporation into microbial biomass; and,*
- *Quantification of 13C enriched dissolved inorganic carbon (DIC), which indicates contaminant mineralization.*

In addition to the PLFA and DIC analyses conducted on the bio-trap sample; DNA will also be extracted from the samples. The DNA extracts will be analyzed by quantifiable polymerase chain reaction (qPCR) methods to identify and quantify sulfate reducing bacteria.

The deployment of the bio-trap samplers for SIP sampling cannot be conducted in groundwater above 140 degrees Fahrenheit. Additionally, the biotraps should not be deployed until sulfate concentrations have reached the test well locations at concentrations significant enough to support zero-order sulfate reduction. Therefore, the timing of the SIP sampling will be determined in the field and based on feedback from field screening and sulfate/COC groundwater analyses and alternate locations may be selected. Depending on the location of the planned SIP sampling, the duration for cooling, and the travel times for the sulfate SIP sampling and analysis is likely to occur between 6 and 12 months following the start of the EBR sulfate additions and pumping."

Replication of ADEQ General Comment 3 (reference ADEQ FPU16-167, Feb. 11, 2016): The plan assumes that site microbial populations will rebound after steam treatment. This population rebound should be confirmed and monitored to ensure that this polishing step progresses as planned and that the degrading microbial population is (and remains) strong enough to achieve the remedial goal. ADEQ recommends stable isotope probe (SIP) analysis to specifically monitor the degrading population, providing information about population size, health, *insitu* target compound biodegradation rates, and possible environmental stressors. It will also definitively prove in-situ target compound bioattenuation.

<u>Evaluation 4:</u> ADEQ Evaluation of Air Force March 15, 2016 Responses (The following evaluation refers to responses related to ADEQ General Comment 6, and Specific Comments 3 and 4 [reference

ADEQ FPU16-167, Feb. 11, 2016]. In general, the cited comments refer to data that suggests a significant fraction of the initial LNAPL remains in the TTZ after SEE shutdown, and is not accounted for in the EBR calculations.)

Simple mass balances demonstrate that these assertions are not valid. Throughout February and March 2016, the mass extraction rate of VOCs in the thermal accelerator (vapor recovery) averaged 1,880 pounds per day and was almost double the average mass extraction rate of LNAPL (1,044 lbs./day). This mass extraction rate did not exhibit a significant decay. In addition, recent measures of LNAPL composition did not show a significant change. Hence, it is impossible for contact between LNAPL and extracted water to be the source of the excess vapor recovery rate. Also, the thermal zone was shrinking during this period, not expanding, such that LNAPL on the perimeter was cooling. Further, the vapor recovery rate of individual compounds exceeds the ambient solubility limit by roughly a factor of 10 based on the water extraction rate. The only possible source of this excess mass is residual LNAPL residing within soils heated to steam temperature. This residual LNAPL mass is almost certainly higher than the assumed mass of LNAPL in the post-SEE TTZ and used in the EBR calculations. Also, the assumed 90% reduction in BTEX+N content is based on experience from other sites; however, no references, citations, or even site names were provided. Experience from this site does not suggest such a reduction.

Excerpts of Air Force Response to Comment (reference Mar. 15, 2015):

(Excerpted AF response to General Comment 6). "*There is ample contact between LNAPL and groundwater to affect dissolved phase BTEX+N concentrations. Therefore, the concentrations of BTEX+N in extracted water do not provide reliable indication of whether the LNAPL sources are within or outside the TTZ.*"

(Excerpted AF response to Specific Comment 3). "*More recent data [NAPL composition] is available but does not show a significant change in composition.*"

(Excerpted AF response to Specific Comment 4). "*Extracted groundwater is mixed with extracted LNAPL in the extraction piping and initial treatment system steps. Therefore, BTEX+N concentrations at the air stripper influent do not effectively differentiate between mass originating inside or outside the TTZ.*"

(Excerpted and paraphrased AF response to Specific Comment 4). "*The 90% reduction [in BTEX+N concentrations in residual LNAPL post-SEE] is based on experience from other sites.*"

<u>Evaluation 5:</u> ADEQ Evaluation of Air Force March 15, 2016 Responses (The following evaluation refers to responses related to ADEQ General Comments 4 and 7, and Specific Comment 13 [reference ADEQ FPU16-167, Feb. 11, 2016]. In general, the site remediation timeframe and Remedial Action Objective (RAO) attainments are not supported by calculations or estimates.

As stated in the Work Plan, the groundwater modeling does not simulate sulfate biodegradation or reduction. The cited sulfate utilization rates appear to be based on current conditions of TEA limited reactions. Whereas during EBR reactions, with an excess of sulfate present, sulfate reactions will be governed by the availability of dissolved contaminants (NAPL dissolution). Flooding the subsurface with sulfate runs the risk of ambient flow sweeping it downgradient if LNAPL dissolution is slow. The utility of modeling the kinetics of dissolution and degradation upfront is to assess if meeting the RAOs in the desired timeframe is even possible under the assumed conditions. Site-specific LNAPL dissolution rates are available from the TEE Pilot Test Evaluation Report and the following reference:

> Mobile, M., et al., *In-Situ Determination of Field-Scale NAPL Mass Transfer Coefficients: Performance, Simulation and Analysis.* Journal of Contaminant Hydrology, 2016. **187**: p. 31-46.

Excerpts of Air Force Response to Comment (reference Mar. 15, 2015):

(Excerpted AF response to General Comment 4). *"The model used in this addendum is an update to the 3D groundwater model that was included in the RD/RAWP. The 3D groundwater model was not used to simulate biodegradation or reduction of the sulfate."*

(Excerpted AF response to General Comment 4). *"The required mass of sulfate per injection well was assessed considering the distribution of contamination and the sulfate-reduction stoichiometry (Appendix A and Appendix F). Based on the sulfate reduction rate-kinetics analysis results (Appendix C) and considering the dispersion simulation results, maintaining a sulfate concentration above 8,000 mg/L (double the half-saturation concentration) will reduce the mass of injected sulfate at a rate of 33 to 75 mg/L per day."*

(Excerpted AF response to General Comment 7). *"Utilizing the model [provided in the RD/RAWP] now to predict the sulfate TEA utilization, LNAPL depletion, and COC decay is possible; however, this step has limited utility."*

(Excerpted AF response to Specific Comment 13). *"3D groundwater model was not used to assess the required mass or dosing of sulfate TEA"*

Closure

ADEQ may add or amend comments if evidence to the contrary of our understanding is discovered; if received information is determined to be inaccurate; if any condition was unknown to ADEQ at the time this document was signed; or if complementary regulatory agencies bring valid and proven concerns to our attention.

Thank you for the opportunity to comment. Should you have any questions regarding this correspondence, please contact me by phone at (602) 771-4121 or e-mail miller.wayne@azdeq.gov.

Sincerely,

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Remedial Projects Section, Waste Programs Division

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